

All-stainless steel sample canisters equipped with SS bellows valves were prepared in extremely clean conditions, and evacuated for grab-sampling in the fields. The inner surface of the canisters was deactivated by either silanization or water-vapor treatment to prevent adsorption of trace constituents during the long-period storage. All the Antarctic samples collected at 500–1000 m NE of Syowa Station were analyzed after 3–15 months at The University of Tokyo.

The concentrations of  $\text{CCl}_2\text{F}_2$  observed in Antarctica in January–February 1982, 1983 and 1985 were 312, 331 and 359 pptv (pptv =  $10^{-12}$  v/v), respectively, and those of  $\text{CCl}_3\text{F}$  were 169, 177 and 194 pptv, respectively. These concentrations observed in Antarctica were 8–10% lower than those observed in the mid-latitude N.H. (Hokkaido,  $40^\circ$ – $45^\circ\text{N}$ ) in accordance with the predominant emission of these halocarbons in the N.H. (>90%) and their delayed diffusion into the Southern Hemisphere across the Intertropical Convergence Zone. The concentration of  $\text{CH}_3\text{CCl}_3$  was about 30% lower in Antarctica (90 pptv in 1985) in accordance with its relatively short atmospheric lifetime due to the reaction with tropospheric OH radicals.

The global concentrations of  $\text{CCl}_2\text{F}_2$  and  $\text{CCl}_3\text{F}$  have increased steadily by 4–5% every year corresponding to their unchanged large amount world-wide releases (total > 700 kilotons/year) and their extremely long lifetimes in the atmosphere exceeding 70 years (probably 80–150 years). Their global concentrations by computer simulation will exceed 1500 pptv ( $\text{CCl}_2\text{F}_2$ ) and 500 pptv ( $\text{CCl}_3\text{F}$ ) in 50 years, and will exceed 3000 pptv and 1000 pptv, respectively, in the steady state even with their current release rates. If the release rates continue to increase as the recent statistics indicates, their atmospheric concentrations will become inevitably higher than those values.

The total Cl-concentration in the troposphere controls the amount of Cl introduced into the stratosphere. The Cl-concentration is estimated to be about 600 pptv in 1900 only due to natural  $\text{CH}_3\text{Cl}$  and may have increased to 1000 pptv in the 1960's and to 1500 pptv in the 1970's according to the increasing release of anthropogenic halocarbons such as  $\text{CCl}_4$ ,  $\text{CCl}_3\text{F}$ ,  $\text{CCl}_2\text{F}_2$ ,  $\text{CH}_3\text{CCl}_3$ , and others. The present Cl-concentration in the atmosphere is calculated to be 3000–3500 pptv with 1000–1500 pptv increase per decade. The Cl-concentration will gradually approach 10000 pptv with current emission rates, or 20000 pptv with increasing emission rates. Under these situations, substantial depletion of stratospheric ozone and greenhouse effect are anticipated. The increment of methane concentration as observed in the both hemispheres will also cause greenhouse effect and depletion of tropospheric OH radicals.

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## DECOMPOSITION OF POLYATOMIC MOLECULES DUE TO AURORAL X-RAYS (ABSTRACT)

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The concentration of carbon monoxide in the Arctic stratosphere measured by a commercial airliner and reported by R. PRATT and P. FALCONER (J. Geophys. Res., **84**, 7876, 1979) showed a specific interesting feature which showed an upward increasing trend together with that of ozone. The feature was not observed in the Antarctic measurement that followed two days later. More interestingly the fine structure of the Arctic measurement showed a feature of sudden tempera-

ture decreases associated with simultaneous increase of carbon monoxide and decrease of ozone. Again no such feature was observed in the Antarctic measurement only showing approximately a constant level of carbon monoxide concentration irrespective of ozone variations.

According to the investigation of the present author a big geomagnetic storm took place immediately before the starting of the Arctic measurement. On the basis of the fact that the binding energy of polyatomic molecules is generally weaker than diatomic molecules in the atmosphere and the electron bombardment has easier access to molecules for excitation and dissociation than photons in low energy regions, the author assumed a scenario of intervening mechanisms as follows: The auroral X-rays penetrated down to the lower stratosphere during magnetic storms, then producing photoelectrons. The electrons in the course of losing energy by collision with air molecules dissociated  $\text{CO}_2$ , thus producing CO. The decrease of  $\text{CO}_2$  and  $\text{O}_3$  in the upper layers will give rise to the temperature decrease of lower layers by way of radiational cooling to space.

The main point of discussion in this paper is the quantitative explanation of the amount of CO increase at the level of observation which is usually supposed to be too low for X-rays to arrive. Population of  $\text{CO}_2$  dissociation was calculated by means of the analytical expression of the yield of secondary electrons deduced by A. E. S. GREEN *et al.* (J. Geophys. Res., **82**, 5101, 1977) and the dissociation cross section of  $\text{CO}_2$  reported by J. L. FOX and A. DALGARNO (Planet. Space Sci., **27**, 491, 1979). Then the number density was calculated with the assumption of the amount of electron precipitation as was considered reasonable from observation. The result turned out to be too small almost by the order more than three. In order that this mechanism works well some kind of amplification is needed. A promising physical mechanism is the intervention of electric field associated with the geomagnetic storm. This will energize the electrons of the whole steps of degradation, thus increasing the number of the slowest electrons by many orders which are essentially supposed to play a main role for the dissociation of polyatomic molecules.

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## SPECTRAL MEASUREMENTS OF THE SOLAR RADIATION AT SYOWA STATION, ANTARCTICA (ABSTRACT)

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Spectral measurements of the solar radiation were performed at Syowa Station, Antarctica, from January 1984 to January 1985 as part of the Antarctic Middle Atmosphere Program by one of the authors (M.S.) as a wintering member of the 25th Japanese Antarctic Research Expedition.

The spectral intensity of direct solar radiation was measured by a sunphotometer (Eko Instruments Co., Model MS-111) which was equipped with eight interference filters at wavelengths  $\lambda = 332, 369, 500, 675, 777, 862, 939$  and  $1048$  nm. Values of the aerosol optical thickness obtained by this sunphotometry were larger than